# CATION EXCHANGE CAPACITY MEASUREMENTS ON ILLITE USING THE SODIUM AND CESIUM ISOTOPE DILUTION TECHNIQUE: EFFECTS OF THE INDEX CATION, ELECTROLYTE CONCENTRATION AND COMPETITION: MODELING

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**Abstract**—The isotope dilution technique using Na and Cs as index cations was used to determine the cation exchange capacity (CEC) of illite du Puy as a function of background electrolyte composition. The work showed, in accord with previous studies, that the CEC values were in the order Cs-CEC > Na-CEC. Sodium is commonly chosen as the index cation in CEC determinations using the isotope dilution method. The experimentally measured Na-CEC values for Na-illite increased from ~75 to ~200 meq kg$^{-1}$ for $NaClO_4$ concentrations in the range $5.6 \times 10^{-4}$ to $1.25 \times 10^{-2}$ M. Cesium CEC determinations showed a much less pronounced trend over a $CsNO_3$ concentration range from $10^{-3}$ to $10^{-2}$ M. A reference Cs-CEC value of 225 meq kg$^{-1}$ was chosen. Careful chemical analyses of the supernatant solutions revealed that Ca and Mg at the (sub)μmolar level were present in all the determinations, despite the extensive conditioning procedures used. Competition between (Ca + Mg) and Na for the exchange sites was put forward as an explanation for the variation of Na-CEC values. This hypothesis was confirmed in a series of single ($^{45}Ca$) and double ($^{45}Ca$ plus $^{22}Na$) labeling experiments. Calcium-sodium selectivity coefficients ($_{Na}^{Ca}K_c$) were calculated from the experimental data for $NaClO_4$ concentrations from $5.6 \times 10^{-4}$ to 0.1 M and exhibited a variation from 1.6 to 14.3. A two-site cation exchange model was developed with site capacities and $_{Na}^{Ca}K_c$ values for each site: planar site capacity =180 meq kg$^{-1}$, $_{Na}^{Ca}K_c^{PS} = 2$; type II site capacity = 45 meq kg$^{-1}$, $_{Na}^{Ca}K_c^{II} = 80$. The model was able to predict the Na and Ca occupancies in the Na-CEC experiments over the whole range of $NaClO_4$ concentrations. It is recommended that Cs should be used instead of Na as the index cation for determining the CEC of illite.

**Key Words**—Cation Exchange Capacity (CEC), Cesium, Illite du Puy, Isotopic Dilution Technique, Two-site Cation-exchange Model.

## INTRODUCTION

Cation exchange is one of the most important properties of clay minerals and CEC one of the main parameters required to understand their behavior. The cation exchange and sorption characteristics of illite have been the subject of numerous publications over the past few decades. This is not surprising as it is a major component in many soils and argillaceous rocks. The former are of interest with respect to the fate of heavy metal contaminants in environmental sciences (*e.g.* Jenne, 1977) and the latter are being viewed with continuing interest in many European waste management programs as suitable host formations for the deep geological disposal of radioactive waste (Horseman *et al*., 1996; NAGRA, 2002).

The existence of different types of exchange sites on illite is well documented. One class of sites, often termed "frayed edge sites" (Jackson, 1968), are predominantly accessible to cations with low hydration energies *e.g.* K, Rb, Cs, NH$_4$ (Sawhney, 1970, 1972; Eberl, 1980; Cremers *et al*., 1988). These sites have high affinities for the above-mentioned cations but the site capacity is low, <1% of the total CEC. Recent nuclear

magnetic resonance (NMR) spectroscopic investigations for Cs sorbed on illite have identified at least two 'chemical environments for Cs' at the surface of the illite crystallites (Kim *et al*., 1996; Kim and Kirkpatrick, 1997). Since it is not possible to detect frayed-edge sites with such techniques (due to their low capacity), the implication is that the sorption of Cs could involve three site types. Indeed, three sites were used by Bolt *et al*. (1963), Brouwer *et al*. (1983) and Bradbury and Baeyens (2000) to describe the K/Cs uptake on Winsum, Morris and du Puy illites, respectively. In their modeling work, the last authors give the distribution of the three site types as: frayed-edge sites = 0.25% CEC, Type II sites = 20% CEC and planar sites = 80% CEC. On the basis of microcalorimetry measurements, Goulding and Talibudeen (1980) suggested that there may be four different exchange sites in illite.

Amongst the many methods developed to measure CEC values, the isotope dilution technique has become very popular and has been used widely over a long period of time (Cremers, 1968; Van Bladel and Menzel, 1969; Maes *et al.*, 1976; Brouwer *et al.*,1983; Bradbury and Baeyens, 2000). The procedure, which is simple, quick and convenient, consists of conditioning the clay to the homo-ionic form of a chosen index cation *e.g.* Na, Ca, and then labeling a suspension in a corresponding background electrolyte, *e.g.* NaClO$_4$, Ca(NO$_3$)$_2$, usually

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at a concentration in the mmolar region. The CEC is calculated from the redistribution of the radiotracer between the solid and liquid phases (Cremers, 1968). As only isotope exchange is involved, equilibrium is usually attained within a few hours.

The main assumptions in the method are that (1) all exchange sites on the clay mineral arising from isomorphous substitution are occupied by the index cation, (2) all such sites are accessible to the radiotracer, (3) exchange is rapid and reversible, and (4) no other site types existing on the surface of the clay are involved.

Although in the majority of cases Na is the preferred index cation, the method has been applied using other monovalent and bivalent cations such as Cs, Sr, Ca and Ba. Ideally it would be expected that the CEC values determined would be independent of the index cation within experimental error, usually estimated to be 5 to 10%. However, this does not appear to be the case in practice, and the literature contains a significant number of reports drawing attention to discrepancies in CEC values measured by the isotope dilution technique using different index cations. Brouwer *et al.* (1983) reported CEC values on illite in the sequence: Na-CEC < K-CEC ⩽ Ca-CEC ⩽ Sr-CEC < Ba-CEC. The measurements of Gorgeon (1994) and Van Bladel and Menzel (1969) on montmorillonite indicate that Na-CEC < Cs-CEC and Na-CEC < K-CEC, respectively. (The differences were up to a factor of 2.)

These discrepancies have been interpreted in different ways at various times. Maes and Cremers (1975) and Maes *et al.* (1976) proposed explanations based on the involvement of pH-dependent edge sites, Maes and Cremers (1977) on non-stoichiometric uptake of bivalent ions at high loading, Sposito *et al.* (1983) on the formation of chloro complexes for cases where a chloride salt provides the background electrolyte, Gorgeon (1994) on there being two exchange-site types, one of which is not available to Na but available to Cs, and Van Bladel and Menzel (1969) on collapsing interlayers. In addition, Cremers and Thomas (1966) and Van Bladel and Menzel (1969) observed a trend in Na-montmorillonite systems such that the measured CEC appeared to increase as the background NaCl electrolyte concentration increased in the range $10^{-3}$ to $10^{-2}$ M.

Because the isotope dilution technique is so convenient, and because reliable exchange data (capacities, cation occupancies, selectivity coefficient values) are essential for understanding clay mineral properties in the spheres of sorption (Bradbury and Baeyens, 2000), and water chemistry (Bradbury and Baeyens, 1998, 2003), the above discrepancies are re-examined in the light of new experimental data and understanding.

The paper deals with two main topics. The first concerns clay mineral sample preparation methodologies and CEC measurements on illite by the isotope dilution technique. One aim here is to recommend a suitable index cation and procedures to obtain reliable CEC values for clay mineral systems. The second aspect, and main focus of this work, deals with the interpretation of the measurements, extraction of selectivity coefficients, modeling and explanations of previously observed inconsistencies in CEC measurements.

The conditioning process applied to illite is an important part of the procedure in the isotope dilution technique and normally involves repeated washings of the clay mineral with relatively highly concentrated solutions of the chosen index cation (*e.g.* Baeyens and Bradbury, 1997; Poinssot *et al.*, 1999a). Ensuring the complete removal of impurity cations, especially Ca, may be more difficult than might be supposed. Calcite is often present as an accessory mineral and a simple calculation for the volumes of washing solution used, normally at neutral pH, would indicate that the quantities are more than sufficient to dissolve, and thus remove, all of the calcite present. However, two further factors need to be considered: Ca may be present in phases other than calcite, and conditioning is usually carried out in a closed system. In the latter case, dissolution of calcite leads to a pH increase (up to pH = 9 or 10) where the solubility is much less than at neutral pH. Also, Ca can undergo exchange reactions on the clay mineral. The result of these processes, unless great care is taken, is that there is residual Ca in the system.

Further preparation of the suspensions involves a peptization procedure and setting the concentration of the background electrolyte. For practical reasons, CEC determinations are carried out at relatively low concentrations; *i.e.* mmolar levels (*e.g.* Cremers, 1968). Dilution of the original washing solution, which is the net effect of these steps, favors the exchange of bivalent cations over monovalent cations (Bruggenwert and Kamphorst, 1982), again making the complete removal of bivalent cations from the system difficult. Finally, the background electrolytes themselves may contain trace levels of bivalent cation impurities (see Table 1).

The important point being made here is that in previous measurements of CEC values using different index cations with varying background electrolyte concentrations and at different pH values, far too little attention has been paid to the influence of aqueous chemistry on the results.

## MATERIALS AND METHODS

### Clay preparation

*Material.* The illite du Puy was collected from the upper regions of an 80 m thick Oligocene geological formation in the region of Le Puy en Velay, France. Samples were crushed in a mechanical crusher, powdered and the ⩽ 63 μm fraction separated using an electric sieve. Both this 'as-received' illite and conditioned illite samples were sent to the French National Institute for Agronomy

Table 1. Chemical analyses (mol $L^{-1}$) of the purified 1 M $NaClO_4$ solution and last conditioning water from the preparation of conditioned Na-illite in $NaClO_4$ at 0.1 and 0.01 M, pH ~7.

| Element | 1 M $NaClO_4$ | Na-illite at 0.1 M $NaClO_4$ | Na-illite at 0.01 M $NaClO_4$ |
|---|---|---|---|
| Si | $1.3 \times 10^{-6}$ | $3 \times 10^{-5}$ | $4 \times 10^{-5}$ |
| Al | $1.0 \times 10^{-6}$ | $3 \times 10^{-6}$ | $5 \times 10^{-6}$ |
| Fe | $<(3 \times 10^{-7})$ | $3 \times 10^{-7}$ | $<(3 \times 10^{-7})$ |
| Mg | $1.0 \times 10^{-6}$ | $3 \times 10^{-6}$ | $2 \times 10^{-6}$ |
| Mn | $1.0 \times 10^{-6}$ | $7 \times 10^{-8}$ | $8 \times 10^{-8}$ |
| K | $1.1 \times 10^{-4}$ | $1.5 \times 10^{-5}$ | $5 \times 10^{-6}$ |
| Ca | $2.0 \times 10^{-6}$ | $10^{-5}$ | $7 \times 10^{-6}$ |
| Ba | $2.0 \times 10^{-7}$ | $2 \times 10^{-7}$ | $<(9 \times 10^{-9})$ |
| Zn | $<(4 \times 10^{-7})$ | $<(4 \times 10^{-7})$ | $5 \times 10^{-7}$ |
| Ni | $<(5 \times 10^{-7})$ | $<(5 \times 10^{-7})$ | $<(5 \times 10^{-7})$ |
| Sr | $3.3 \times 10^{-7}$ | $5 \times 10^{-8}$ | $\sim 10^{-8}$ |
| P | $< (10^{-6})$ | $10^{-5}$ | $10^{-5}$ |
| S | $<(2 \times 10^{-6})$ | $<(2 \times 10^{-6})$ | $<(2 \times 10^{-6})$ |

The numbers given in parentheses are 'reliable detection limits' which are taken to be 10 times higher than the ICP-AES detection limits. The elements Pb, Co, Cd, Cu, Rb, Cs, Hg could not be detected and were therefore below the ICP-OES detection limits ($<10^{-8}$ M).

Research, Laboratory for Soil Science (Versailles, France) for mineralogical analysis. A combination of X-ray diffraction (XRD) investigations and bulk chemical analyses revealed that the 'as-received' material contained ~74 wt.% illite and kaolinite, ~20 wt.% calcite (with some siderite) and small amounts of quartz (5 wt.%), whereas the conditioned illite comprised only illite (~93 wt.%) and kaolinite (~7 wt.%). Chlorite, smectite, mixed-layer clays and calcite (and other Ca phases) were not detected. Kaolinite will make a contribution to the measured CEC. However, the CEC of kaolinite is low (*e.g.* ~60 meq $kg^{-1}$, Goulding and Talibudeen, 1980) and at a content of 7 wt.% would contribute only ~2% to the total measured value.

*Conditioning of illite du Puy.* All of the background electrolyte solutions were prepared from Fluka 'suprapur' grade chemicals and ultra-pure de-ionized water (resistivity ~18 MΩ cm). The solutions were purified using the methodology given in Baeyens and Bradbury (1997) which resulted in decreases in impurity levels by a factor of 10 to 100 depending on the particular metal.

The clay preparation method as described by Cremers and Thomas (1966) was used. The purifying procedure was applied to the 'as-received' powder so as to obtain, as far as possible, a single phased suspension of Na-illite in a 1:1 background electrolyte for the CEC measurements and sorption investigations. 100 g quantities of the illite powder were contacted with ~2 L of a purified 1 M $NaClO_4$ solution (see Table 1), shaken end-over-end for several hours and allowed to flocculate overnight before decanting off the supernatant solution. This procedure was repeated three times, which was sufficient to convert the clay to the homo-ionic Na-form.

Separation of the <0.5 μm Na-illite fraction was achieved by dividing the 2 L suspension into 12 250 mL centrifuge bottles which were then filled with de-ionized water which had been previously pre-equilibrated with a small quantity of conditioned illite (~20 mg $L^{-1}$). After allowing the illite to peptize for ~15 min and centrifuging for ~7 min at ~600 g max, the Na-illite fraction in the supernatant suspension (<0.5 μm) was transferred into a large polyethylene container. A fresh 1 M $NaClO_4$ solution was then immediately added in order to flocculate the fine clay particles and to prevent hydrolysis. After repeating the whole procedure ~20 times, a yield of ~35 wt.% of peptized illite was achieved. The resulting stock suspension (~6 g $L^{-1}$ of Na-illite in ~0.4 M $NaClO_4$), was stored in the dark at 4ºC and was never kept for longer than 6 months.

In the previous washing procedure with de-ionized water it is unavoidable that the illite hydrolyzes to some extent, which may result in the precipitation of metal hydroxy compounds. In order to remove such unwanted secondary phases, the procedure described by Maes and Cremers (1975) was used. 2 L of the stock suspension were taken and acidified to pH ~3.5 with $HNO_3$ and left for 1 h. Thereafter, the suspension was centrifuged (7 min at 600 g. max), the supernatant liquid decanted off and the clay re-suspended and neutralized in a 1 M $NaClO_4$ solution. The clay content in the suspensions was determined by weighing and evaporation to constant weight at 105ºC. Salt corrections were made by treating the last conditioning solution simultaneously in the same manner.

Batches were prepared at various ionic strengths (~$5 \times 10^{-4}$ M to ~$10^{-2}$ M $NaClO_4$) from the stock suspension for the CEC experiments. This was achieved by placing 35 mm diameter dialysis bags, each containing ~75 mL of the Na-illite stock suspension, in a 1 L polyethylene flask filled with the desired concentration of the $NaClO_4$ solution. The flask was shaken end-over-end for ~3 h. This procedure was repeated until the electrical conductivity of the equilibrium solution was

Table 2. Summary of Na-CEC measurements by the isotopic dilution method.

| Experiment | Na conc. (M) | Na-CEC (meq kg$^{-1}$) | Number of measurements | Mg conc. (M) | Ca conc. (M) |
|---|---|---|---|---|---|
| Na-1 | $5.6 \times 10^{-4}$ | 75 | 3 | NM | $1.2 \times 10^{-6}$ |
| Na-2 | $1.0 \times 10^{-3}$ | 124 | 6 | NM | NM |
| Na-3 | $3.0 \times 10^{-3}$ | 150 | 3 | NM | $1.9 \times 10^{-6}$ |
| Na-4 | $5.0 \times 10^{-3}$ | 185 | 3 | NM | NM |
| Na-5 | $1.0 \times 10^{-2}$ | 171 | 3 | NM | $6.0 \times 10^{-6}$ |
| Na-6 | $1.0 \times 10^{-2}$ | 188 | 9 | NM | NM |
| Na-7 | $1.25 \times 10^{-2}$ | 205 | 3 | $3.8 \times 10^{-7}$ | $2.3 \times 10^{-6}$ |
| Na-8 | $1.25 \times 10^{-2}$ | 198 | 3 | $1.8 \times 10^{-7}$ | $2.2 \times 10^{-6}$ |
| Na (low Ca)-1 | $2.1 \times 10^{-3}$ | 187 | 3 | $1.3 \times 10^{-7}$ | $3.3 \times 10^{-7}$ |
| Na (low Ca)-2 | $2.3 \times 10^{-3}$ | 190 | 3 | $1.3 \times 10^{-7}$ | $3.7 \times 10^{-7}$ |

For Na-1, Na-3 and Na-5 the Ca concentrations were not directly measured but were calculated from the $R_d$-Ca measured in the $^{45}$Ca single labeling experiments. The $R_d$-Ca values are given in Table 4.
For Na-7, Na-8, Na(low Ca)-1 and Na(low Ca)-2 the Mg and Ca concentrations given are measured values.
NM = not measured

the same as the original solution, indicating that the conditioning process was completed, generally after five exchange cycles. The Na concentrations in the final conditioning solutions were analyzed by plasma-emission spectroscopy (Varian Vista AX CCD Similtanes ICP-OES). Typical examples of the water chemistries from the preparation of such illite batches are given in Table 1 for Na-illite.

In the cases where a Cs-illite was required, exactly the same conditioning procedure was used except that CsNO$_3$ was used instead of NaClO$_4$.

*CEC and sorption measurements*

In order to be able to understand the measured CEC values and model the exchange behavior of illite, it was necessary to perform different types of experiments: (1) CEC measurements as a function of background electrolyte concentration using the Na and Cs isotope dilution technique (see section below); and (2) sorption experiments using double labeling ($^{22}$Na and $^{40}$Ca) and single labeling ($^{45}$Ca) carried out under the same conditions as the Na-CEC determinations (see 'Results and Discussion' section).

*CEC determinations by the Na and Cs isotope dilution techniques.* The isotope dilution technique was used to measure the CEC of purified illite du Puy using Na and Cs as index cations. Sodium and Cs CEC measurements were carried out over a range of NaClO$_4$ and CsNO$_3$ solution concentrations respectively, $\sim 5 \times 10^{-4}$ to $\sim 10^{-2}$ M.

For the CEC determinations, aliquots of suspensions were equilibrated over at least 3 days with $^{22}$Na or $^{134}$Cs labeled final conditioning solutions at the appropriate concentration. Three days was deemed sufficiently long to attain exchange equilibrium as a previous kinetic study by Poinssot *et al.* (1999a) showed no significant changes in CEC values over a period of 21 days. At the

end of this time, the samples were centrifuged (95,000 g (max) for 1 h), the activity in solution was measured by gamma spectrometry and the pH was determined (~7). The CEC values were calculated from the initial and final activities in solution.

Note that in order to obtain reproducible results, the experimental set up had to be arranged such that the 'moles' of index cation in solution were approximately twice the 'moles' of the corresponding cation on the illite. This implied that a higher background concentration required a greater quantity of illite. For example, solid to liquid (S:L) ratios of ~2 g L$^{-1}$ and ~20 g L$^{-1}$, respectively, were required for $5 \times 10^{-4}$ M and $10^{-2}$ M electrolyte solution concentrations. The experiments rapidly become impractical at background electrolyte concentrations >$10^{-2}$ M because of the large quantities of illite required. Estimated CEC measurement errors were ~10 meq kg$^{-1}$.

RESULTS AND DISCUSSION

The results of the Na- and Cs-CEC measurements are summarized in Tables 2 and 3, respectively. The results in Table 2 show clearly that an increase in Na concentration in the background electrolyte leads to an increase in the measured Na-CEC values. The hypothesis put forward to explain this behavior is that Ca and Mg,

Table 3. Summary of Cs-CEC measurements by the isotopic-dilution method.

| Experiment | Cs concentration (M) | Cs-CEC (meq kg$^{-1}$) | No. of measurements |
|---|---|---|---|
| Cs-1 | $1.0 \times 10^{-3}$ | 196 | 8 |
| Cs-2 | $3.0 \times 10^{-3}$ | 216 | 4 |
| Cs-3 | $5.0 \times 10^{-3}$ | 225 | 20 |
| Cs-4 | $1.0 \times 10^{-2}$ | 240 | 8 |

which were present in all of the experiments (see columns 5 and 6 in Table 2) influenced the Na-CEC determinations. Both of these bivalent cations occupy exchange sites on the Na-illite. The measured Na-CEC reflects only the Na occupancy on the clay. Under such circumstances, Na-CEC determinations are predestined to underestimate the exchange capacity. As the Na background concentration increases, Na is capable of displacing increasing amounts of Ca and Mg from the exchange sites on illite, thus leading to higher Na occupancies which are reflected in a higher Na-CEC value. However, the Na concentration is not the only factor involved: the (Ca + Mg) levels in solution also play an important role, because under a given set of conditions they will determine the bivalent occupancy level on the clay mineral. This is particularly so at the most commonly used Na salt concentrations of $\sim 10^{-3}$ M used in CEC determinations. Here, the "valency effect" (Bruggenwert and Kamphorst, 1982), favors the uptake of bivalent ions.

During the conditioning process of a Na-illite to produce a Cs-illite, Cs is capable of displacing Ca and Mg from the exchange sites even at low concentrations since the selectivity of Cs with respect to bivalent cations is much greater than that of Na. Thus, in a Cs-conditioned clay there is less Ca and Mg on the clay than for a Na-clay under the same conditions. Consequently, the Cs-CEC exhibits less variation in the concentration range of practical importance. The results of the Cs-CEC determinations given in Table 3 thus provide a better reflection of the true CEC of illite than the Na measurements. On the basis of the data in Table 3, a reference CEC value of 225±10 meq kg$^{-1}$ was chosen.

The hypothesis arising from these considerations is that the difference between the two determinations, Cs-CEC and Na-CEC, is the (Ca+Mg) occupancy on the clay. In order to test this hypothesis and obtain quantitative information on (Ca+Mg) occupancies in CEC determinations, double ($^{22}$Na and $^{45}$Ca) and single ($^{45}$Ca) labeling experiments were performed. These tests, and the results, are described below.

First, an initial test was made. As mentioned previously, conditioning in a closed system in which calcite is present leads to a pH increase (up to pH = 9 or 10) where carbonate solubilities are much less than at neutral pH. Lower solubilities under such circumstances may also apply when Ca is present in phases in addition to calcite. In order to try to reduce the residual Ca/Mg in the system, a modified procedure was adopted in which the pH was maintained at values below 6 throughout the conditioning step with 1 M NaClO$_4$ by periodically checking the pH and adjusting where necessary with 1 M HNO$_3$. After completion of the conditioning, the Na-CEC values were determined as described above. For samples Na (low Ca)-1 and Na (low Ca)-2, the Ca and Mg concentrations were reduced to low $10^{-7}$ M levels.

As can be seen from Table 2, the measured Na-CEC values are significantly larger than in previous measurements performed at comparable NaClO$_4$ concentrations in which the normal conditioning process was used. These results are in accord with the Ca/Mg competition hypothesis.

### Double ($^{22}$Na and $^{45}$Ca) and single ($^{45}$Ca) labeling experiments

In the following it will be shown that the CEC measured by the Na-isotope dilution experiment depends sensitively on the Na and Ca equilibrium concentrations in the aqueous phase. Within the usual mmolar range of Na concentrations used in CEC determinations, it only requires the presence of μmolar quantities of bivalent ions (principally Ca and Mg) to falsify the measurements.

*Double ($^{22}$Na and $^{45}$Ca) labeling experiments.* For these tests the Na (low Ca)-1 material (Table 2) was chosen. A Na-CEC of 187 meq kg$^{-1}$ was determined (triplicate samples) in a $2.1 \times 10^{-3}$ M NaClO$_4$ background electrolyte. (The background concentrations of Mg and Ca were $1.3 \times 10^{-7}$ M and $3.3 \times 10^{-7}$ M, respectively.) If the Cs-CEC value of 225 meq kg$^{-1}$ (see above) is taken to be the 'true' CEC, this implies that the Ca+Mg occupancy on this particular sample of conditioned illite must be approximately 38 meq kg$^{-1}$. (This number will be used in the mass-balance calculations given below.)

Double labeling experiments were subsequently performed with the conditioned clay suspension above by taking 20 mL aliquots and adding to them 10 mL of a $7.5 \times 10^{-4}$ M Ca(NO$_3$)$_2$ solution labeled with $^{22}$Na and $^{45}$Ca in polypropylene centrifuge tubes (S:L ratio = 6.3 g L$^{-1}$). The initial cation concentrations in the suspensions were thus: [Na] = $1.4 \times 10^{-3}$ M and [Ca] = $2.5 \times 10^{-4}$ M. (The presence of the very low Mg concentrations compared to Ca can be ignored in the following data analysis.) The experiments were carried out in triplicate. Note that in sorption experiments it is important to define the initial conditions as well as possible. The original suspension was not simply taken and labeled because of the uncertainties in the exact values of the very low Ca and Mg concentrations. Instead, the Ca concentration in the experiments was defined through the addition of the 10 mL of double-labeled solution.

The double labeling experiments are essentially simultaneous sorption tests with $^{22}$Na and $^{45}$Ca. The sorption methodology is described in detail in Baeyens and Bradbury (1997). Briefly, the tubes were shaken end-over-end for 3 days before centrifuging for 1 h at 95,000 g (max) and the supernatant solutions were radio-assayed using a Canberra Packard Cobra 5003 Auto Gamma Counter for $^{22}$Na and a Canberra Packard Tri-Carb 2250CAB Liquid Scintillation Counter for $^{45}$Ca. The average distribution ratios determined for Na and Ca in the triplicate determinations were 60.5 L kg$^{-1}$ and 22920 L kg$^{-1}$, respectively (see Table 4).

Table 4. Results of double ($^{22}$Na and $^{45}$Ca) and single ($^{45}$Ca) labeling experiments.

| Na equilibrium conc. (M) | $R_d$-Na (L kg$^{-1}$) | $R_d$-Ca (L kg$^{-1}$) | Na sorbed (meq kg$^{-1}$) | Ca sorbed (meq kg$^{-1}$) | Ca equilibrium conc. (M) |
|---|---|---|---|---|---|
| [#]$1.9 \times 10^{-3}$ | 60.5 | 22920 | *115 | **115 | $2.5 \times 10^{-6}$ |
| $1.0 \times 10^{-2}$ | | 4500 | 171 | [†]54 | [$]$6.0 \times 10^{-6}$ |
| $3.0 \times 10^{-3}$ | | 19740 | 150 | [†]75 | [$]$1.9 \times 10^{-6}$ |
| $5.6 \times 10^{-4}$ | | 62500 | 75 | [†]150 | [$]$1.2 \times 10^{-6}$ |

[#] Double labeling experiment
* Calculated from: $R_d$-Na·Na equilibrium concentration (and converted to meq kg$^{-1}$)
** Calculated from: $R_d$-Ca·Ca equilibrium concentration (and converted to meq kg$^{-1}$)
[†] Calculated from: [225 − (Quantity of Na-sorbed)] (meq kg$^{-1}$)
[$] Calculated from: [Quantity of Ca-sorbed]/[$R_d$-Ca] (M)

Direct measurements of the equilibrium Na and Ca concentrations could not be made because the supernatant solutions were radioactive. Instead, these concentrations were calculated from mass balance considerations using:

$$V(Ca)_{add.} + mI_{Ca} = mR_d(Ca)_{eq.} + V(Ca)_{eq.} \quad (1)$$

where:

$V$ = volume (L),
$(Ca)_{add.}$ = concentration of Ca added,
$m$ = mass of illite (kg),
$I_{Ca}$ = initial Ca loading on the illite (mol kg$^{-1}$),
$R_d$ = distribution coefficient (L kg$^{-1}$),
$(Ca)_{eq.}$ = Ca equilibrium concentration (M).

The initial loadings of Na, $I_{Na}$ and Ca, $I_{Ca}$, on the clay were taken to be 187 and 19 mmol kg$^{-1}$, respectively (see above). The results of the calculations using a Na loading of 187 meq kg$^{-1}$, and with the assumption of a 38 meq kg$^{-1}$ Ca initial loading on the clay, yielded equilibrium Na and Ca concentrations of $1.9 \times 10^{-3}$ M and $2.5 \times 10^{-6}$ M, respectively. (Note that the equilibrium Na concentration is higher than the initial value because Na has been displaced by Ca from the clay. Likewise, the Ca equilibrium concentration is lower than the initial value because Ca has been taken up by the illite.)

The measured distribution ratios and the equilibrium concentrations determined from mass-balance considerations allow the quantities of Na and Ca on the clay to be calculated independently. The calculated quantity of Na on the clay is ~115 meq kg$^{-1}$ and the amount of Ca is ~115 meq kg$^{-1}$, giving a sum of 230 meq kg$^{-1}$. This is in good agreement with the reference Cs-CEC value of 225 meq kg$^{-1}$. This result adds considerable credence to the hypothesis that the discrepancy between Cs-CEC and Na-CEC values can be explained by the presence of Ca which is not displaced in the determinations based on Na as an index cation.

*Single ($^{45}$Ca) labeling experiments.* Sorption experiments with $^{45}$Ca tracer were carried out on aliquots of the same clay suspensions used for the determinations of Na-CEC

values at NaClO$_4$ concentrations of $5.6 \times 10^{-3}$ M (Na-1), $3 \times 10^{-3}$ M (Na-3) and $1.0 \times 10^{-2}$ M (Na-5) reported in Table 2. The methodology was essentially the same as described above. The results of the $R_d$-Ca measurements are presented in Table 4. The chemistries of Ca and Mg are so similar that identical behaviors can be assumed to a good first approximation. The equilibrium concentration of Ca in the experiment was calculated from the quotient of the quantity of Ca sorbed (in mol kg$^{-1}$) and the measured Ca distribution ratio (in L kg$^{-1}$).

The Na concentrations, the quantity of Na on the clay (equivalent to the Na-CEC values previously determined) and the distribution ratio for Ca, $R_d$-Ca ($=R_d$(Ca+Mg)) are measured quantities. If the hypothesis given in the previous section is correct, then the quantity of Ca+Mg on the clay should be given by the Cs-CEC minus the Na-CEC in each of the systems measured, column 3 in Table 2. Using the measured $R_d$-Ca values and the quantities of (Ca+Mg) on the clay, enables (Ca+Mg) aqueous concentrations to be calculated (column 6, Table 4).

### Selectivity coefficients

*Selectivity coefficient calculations from the Na-CEC data.* From the Na-CEC results given in Table 2 and the double-labeling experiment (Table 4), eight sets of data can be selected for which Mg and Ca equilibrium concentrations are available. For these systems, Ca-Na selectivity coefficients ($K_c$) for illite can be calculated under the individual experimental conditions over a range of NaClO$_4$ concentrations from $5.6 \times 10^{-4}$ M to $1.25 \times 10^{-2}$ M using equation 2 (Gaines and Thomas, 1953),

$$\prescript{Me}{Na}{K_c} = \frac{N_{Me}}{(N_{Na})^2} \cdot \frac{[(Na)\gamma_{Na}]^2}{(Me)\gamma_{Me}} \quad (2)$$

where

Me = (Ca + Mg)

$$N_{Me} = \frac{\text{quantity Me sorbed (meq kg}^{-1})}{\text{CEC (meq kg}^{-1})}$$

Table 5. Summary of selectivity coefficient calculations from Na-CEC data and Sr sorption data.

| Experiment | Na-CEC (meq kg$^{-1}$) | Na conc. (M) | Mg conc. (M) | Ca conc. (M) | $^{Me}_{Na}K_c$ |
|---|---|---|---|---|---|
| Na-1 | 75 | $5.6 \times 10^{-4}$ | – | $1.2 \times 10^{-6}$ | 1.6 |
| Double lab. | 115 | $1.9 \times 10^{-3}$ | – | $2.5 \times 10^{-6}$ | 3.0 |
| Na(low Ca)-1 | 187 | $2.1 \times 10^{-3}$ | $1.3 \times 10^{-7}$ | $3.3 \times 10^{-7}$ | 2.9 |
| Na(low Ca)-2 | 190 | $2.3 \times 10^{-3}$ | $1.3 \times 10^{-7}$ | $3.7 \times 10^{-7}$ | 2.9 |
| Na-3 | 150 | $3 \times 10^{-3}$ | – | $1.9 \times 10^{-6}$ | 4.0 |
| Na-5 | 171 | $1.0 \times 10^{-2}$ | – | $6 \times 10^{-6}$ | 8.5 |
| Na-7 | 205 | $1.25 \times 10^{-2}$ | $1.8 \times 10^{-7}$ | $2.2 \times 10^{-6}$ | 7.6 |
| Na-8 | 198 | $1.25 \times 10^{-2}$ | $3.8 \times 10^{-7}$ | $2.3 \times 10^{-6}$ | 12.4 |
| $R_d$-Sr | – | $1.0 \times 10^{-2}$ | $2.0 \times 10^{-6}$ | $7.0 \times 10^{-6}$ | 9.3 |
| $R_d$-Sr | – | $1.0 \times 10^{-1}$ | $3.0 \times 10^{-6}$ | $2.0 \times 10^{-5}$ | 14.3 |

The results for samples Na-2, Na-4 and Na-6 are not included because (Ca + Mg) background concentrations were not measured, nor could they be calculated.

$$N_{Na} = \frac{\text{quantity Na sorbed (meq kg}^{-1})}{\text{CEC (meq kg}^{-1})}$$

( ) represent molar concentrations,
γ are solution-activity coefficients.

The results are summarized in Table 5, together with the values derived from the Sr-sorption measurements (see below). (Note that in the above calculations the solution activity coefficients were calculated using the Davies equation (Davies, 1962) with a value of 0.3 for the $C_D$ constant.)

The selectivity coefficients calculated at similar NaClO$_4$ concentrations are in reasonable agreement with one another; however, there is a clear systematic trend in the data in that the selectivity coefficient increases with increasing NaClO$_4$ concentration. The difference between the smallest value, 1.6 at $5.6 \times 10^{-4}$ M NaClO$_4$ and the largest value of 14.3 at 0.1 M NaClO$_4$ is almost one order of magnitude. In the modeling section, a possible explanation for this discrepancy is explored.

*Selectivity calculations from Sr sorption data.* From some previous work by Poinssot *et al.* (1999a), distribution ratios for Sr, $R_d$-Sr, were extracted at pH = 7 from the sorption edge plots (log $R_d$-Sr *vs.* pH) measured at trace Sr concentrations in 0.1 M and 0.01 M NaClO$_4$ on Na-illite. The data are summarized in

Table 6. Sr distribution ratios, $R_d$-Sr, together with Ca and Mg concentrations measured in the liquid phase at 0.01 and 0.1 M NaClO$_4$ at pH = 7.

| | 0.01 M NaClO$_4$ | 0.1 M NaClO$_4$ |
|---|---|---|
| $R_d$-Sr, (L kg$^{-1}$) | 3980 | 100 |
| Ca concentration (M) | $7.0 \times 10^{-6}$ | $2.0 \times 10^{-5}$ |
| Mg concentration (M) | $2.0 \times 10^{-6}$ | $3.0 \times 10^{-6}$ |
| Occupancy of M (meq kg$^{-1}$) | 72 | – |
| Occupancy of Na (meq kg$^{-1}$) | 153 | – |
| $^{M}_{Na}K_c$ | 9.3 | 14.3 |

Table 6. At neutral pH, the principal impurity cations in solution arising from the interaction between the Na-illite and the background electrolyte are Mg and Ca. The chemistries of these two elements are so similar to Sr that, to a good first approximation, the three cations can be treated the same, *i.e.* the sorption of Sr, Ca and Mg is essentially the same. The distribution ratio for Sr measured at trace concentrations is determined by the concentrations of (Ca+Mg) in solution and their respective selectivity coefficients, which, again, for chemical analogy reasons, can be taken as being the same (Ca ≡ Mg ≡ Sr ≡ M).

At 0.01 M NaClO$_4$ the occupancy of (Ca+Mg) can be calculated at pH = 7 from the sum of the Ca and Mg concentrations and the Sr distribution ratio, Table 7. If the calculated occupancy of ~72 meq kg$^{-1}$ is used with a Cs-CEC of 225 meq kg$^{-1}$ for illite (see above), a selectivity coefficient for M-Na exchange of 9.3 can be obtained from equation 2.

At 0.1 M NaClO$_4$ and pH = 7, the loadings of bivalent ions are so low that they cannot be calculated with any accuracy from the solution chemistry and sorption data; the fractional occupancy of Na ($N_{Na}$) is approximately unity. Under these circumstances equation 3 can be used to calculate the selectivity coefficient directly (*e.g.* Bradbury and Baeyens, 1994).

$$^{M}_{Na}K_c = 2R_d \cdot M \cdot \frac{1}{\text{CEC}} \cdot \frac{(\gamma_{Na})^2}{\gamma_M} \cdot (Na)^2 \qquad (3)$$

For an $R_d$-Sr value of 100 L kg$^{-1}$, Table 6, a CEC of 0.225 eq kg$^{-1}$, the calculated $^{M}_{Na}K_c$ is 14.3.

*Modeling cation exchange on illite*

*A two-site cation-exchange model for illite.* The selectivity coefficients for Ca-Na exchange given in the previous sections were calculated in the standard manner assuming that only one type of exchange site, the planar sites, is involved. However, proceeding in this manner results in a systematic increase in the calculated

selectivity coefficients by up to almost an order of magnitude as the background electrolyte concentration increases. This has been observed elsewhere in montmorillonite systems (see for example Maes and Cremers, 1986). At the moment there is no generally accepted explanation for this trend. If cation exchange reactions are included in sorption or water chemistry calculations the only options open are either to use an 'averaged selectivity coefficient' or to measure the selectivity coefficient under the specific conditions related to the system in question. In many cases either of these options would yield acceptable results. However, this approach leaves something to be desired in the longer term where system understanding should be the priority.

An alternative way to analyze CEC data is to consider that the capacity is made up of the sum of the contributions from two site types instead of one. Thus the CEC measured for any particular reference cation depends on its selectivity coefficients on the two sites and the chemistry in the background electrolyte.

Obviously, increasing the number of potential exchange sites from one to two increases the complexity of the system and the number of free parameters which can be used in the modeling. This can only be defended if a greater system understanding is achieved and allows the data to be modeled in a more consistent manner over a wider range of conditions.

In the sorption literature, the idea of two (or more) site types invoked to explain characteristics of the cation uptake behavior on illite is not new (Tamura and Jacobs, 1960; Bolt *et al.*, 1963; Sawhney, 1972; Brouwer *et al.*, 1983; Poinssot *et al.*, 1999b). In their recent work, modeling the non-linear sorption behavior of Cs on Na-illite and argillaceous rocks, Bradbury and Baeyens (2000) proposed that the CEC is split 20% to 80% into so-called type II sites (II) and planar-type sites (PS). For the conditioned illite system being considered here with a CEC of 225 meq kg$^{-1}$, this would imply a type II site capacity of ~45 meq kg$^{-1}$ and a planar-site capacity of ~180 meq kg$^{-1}$.

In the CEC determinations on conditioned illite, Ca and Mg were always present. The proposal that the differences between the Na-CEC as a function of background electrolyte concentration and the true CEC (~225 meq kg$^{-1}$) was due to (Ca + Mg) occupancies, was point-wise confirmed above.

At the lowest Na concentrations used ($5.6 \times 10^{-4}$ M) the measured Na-CEC was only ~75 meq kg$^{-1}$ and even under the more usual measurement conditions (mmolar Na, μmolar Ca + Mg), the Na-CEC values were always <180 meq kg$^{-1}$. Only at the very highest Na concentrations did the Na-CEC measurements exceed 200 meq kg$^{-1}$, still less than the corresponding Cs-CEC.

The above considerations led to the working hypothesis that in a Na-conditioned illite the planar type sites (capacity ~180 meq kg$^{-1}$) are predominantly occupied by Na while (Ca+Mg) are mainly occupying the type II sites (capacity ~45 meq kg$^{-1}$).

The modeling approach adopted was to first estimate selectivity coefficients analytically for each site type separately using equation 2. For the lowest Na concentration of $5.6 \times 10^{-4}$ M, it was assumed, to a first approximation, that the bulk of the Na on the exchange sites (given by the Na-CEC value of 75 meq kg$^{-1}$, Table 2) should be on the planar-type sites, the rest being (Ca+Mg). (The Na concentration is not sufficiently high to compete effectively with the Ca on the type II sites.)

This yielded a first estimate for $^{Me}_{Na}K_c^{PS}$ of ~0.9 (Me = Ca + Mg as before)

This value was calculated with respect to the planar-site capacity of 180 meq kg$^{-1}$.

At the highest concentration of $1.25 \times 10^{-2}$ M NaClO$_4$ for which reliable occupancy data are available, the approximation is made that the planar sites are saturated. The difference between the measured average CEC (202 meq kg$^{-1}$) and the planar-site capacity, *i.e.* 180 meq kg$^{-1}$ gives the quantity of Na on the type II sites, *i.e.* 22 meq kg$^{-1}$. Hence the occupancy of Ca is: 45−22 = 23 meq kg$^{-1}$.

Again using equation 2, with a CEC (type II) capacity of 45 meq kg$^{-1}$, yields an estimate for the $^{Me}_{Na}K_c^{II}$ of ~167.

These estimated selectivity coefficients were used as starting input values for the geochemical code MINSORB (Bradbury and Baeyens, 1997) in which the Na and Ca occupancies on both the planar and type II sites were calculated simultaneously. Iterations were carried out to yield the calculated total Na loadings, equivalent to the measured Na-CEC values. The two values for the Ca-Na selectivity coefficients which were best able to reproduce all of the measured CEC values in Table 2 over the whole of the range of experimental conditions used are:

$^{Me}_{Na}K_c^{PS} = 2;$ planar sites

$^{Me}_{Na}K_c^{II} = 80;$ type II sites

The reason that the above selectivity coefficient values are different from the initial estimates is that Ca sorbs on both planar and type II sites under most conditions, and not exclusively on type II sites as assumed.

The calculated total Na loadings are compared with the measured Na loadings from the Na-CEC experiments in Table 7. The calculated Na loadings on the planar and type II sites are also given. As can be seen, calculated and measured values agree within ±10% or better (except for Na-1), which, considering that the error on the measured values may be between ±5 and ±10%, is considered to be very good.

In order to complete the picture, the measured Sr distribution ratios at pH = 7 in 0.1 and 0.01 M NaClO$_4$ can be used to calculate the bivalent cation loadings with the (Ca+Mg) concentrations. The sorbed Na can be

Table 7. Comparison of the measured Na-loadings (Na-CEC values) and those calculated from the two-site model for illite.

| Experiment | —— Experimental results —— | | | —————— Model predictions —————— | | |
| | Na conc. (M) | Ca + Mg conc. (M) | Na sorbed PS + II (meq/kg) | Na sorbed PS + II (meq/kg) | Na sorbed PS (meq/kg) | Na sorbed II (meq/kg) |
| --- | --- | --- | --- | --- | --- | --- |
| Na-1 | $5.6 \times 10^{-4}$ | $1.3 \times 10^{-6}$ | **75** | **59** | 56 | 3 |
| Double lab. | $1.9 \times 10^{-3}$ | $2.5 \times 10^{-6}$ | **115** | **110** | 104 | 6 |
| Na(low Ca)−1 | $2.1 \times 10^{-3}$ | $4.6 \times 10^{-7}$ | **187** | **170** | 156 | 14 |
| Na(low Ca)−2 | $2.3 \times 10^{-3}$ | $5.0 \times 10^{-7}$ | **190** | **173** | 158 | 15 |
| Na-3 | $3.0 \times 10^{-3}$ | $1.9 \times 10^{-6}$ | **150** | **150** | 140 | 10 |
| Na-5 | $1.0 \times 10^{-2}$ | $6.0 \times 10^{-6}$ | **171** | **183** | 165 | 18 |
| Na-7 | $1.25 \times 10^{-2}$ | $2.7 \times 10^{-6}$ | **205** | **202** | 175 | 27 |
| Na-8 | $1.25 \times 10^{-2}$ | $2.4 \times 10^{-6}$ | **198** | **204** | 176 | 28 |
| Rd-Sr | $1.0 \times 10^{-2}$ | $9.0 \times 10^{-6}$ | **153** | **175** | 160 | 15 |
| Rd-Sr | $1.0 \times 10^{-1}$ | $2.3 \times 10^{-5}$ | **220** | **221** | 180 | 41 |

calculated by difference from the 225 meq kg⁻¹ CEC and compared with the model predictions by assuming the chemical analogy mentioned above. The results in Table 7 illustrate that the agreement is satisfactory.

Although the two-site cation-exchange model approach provides insight into the processes occurring in CEC measurements in the illite system and provides explanations for (1) the differences in CEC values when different index cations are used' (2) the dependency on background electrolyte concentration, (3) the varying values of $K_c$ measured as a function of background electrolyte concentration, and (4) the importance of the inherent aqueous impurities in the measurement systems, it is a more complicated model and may not always be easy to apply.

The main difficulty is an obvious one: deciding for a specific illite/aqueous phase configuration how a particular metal ion that undergoes cation exchange distributes between the planar and type II sites. There appears to be no obvious general answer to this question. The only exceptions to this are K, Rb, Cs, NH₄ (*e.g.* Brouwer *et al.*, 1983; Cremers *et al.*, 1988; De Preter, 1990; Poinssot *et al.*, 1999b; Bradbury and Baeyens, 2000) and Ca and its bivalent chemical analogues, Mg and Sr in this work. The use of a two-site exchange model may be important in water chemistry studies where illite is a major system component and the surface occupancies of alkali and alkali earth metals Cs, Na, K, Mg, Ca, Sr are relevant issues.

*Modeling the effect of residual Ca concentrations on Na-CEC values.* As stated previously, in CEC determinations by the Na isotope dilution technique, the aqueous phase concentrations of the suspensions are seldom measured, and even if they are, 'trace' levels of Ca below $10^{-5}$ M are often considered to be of no particular significance.

In order to estimate the effect of low levels of alkali earth metals such as Ca and Mg on CEC determinations by the Na isotope dilution technique in illite systems, calculations were made with the two-site model and the

Ca-Na selectivity coefficient values for planar and type II sites given in the previous section. Table 8 shows the calculated Na-CEC values as a function of Na conditioning concentrations in the range $10^{-3}$ to $10^{-1}$ M and background Ca concentrations from $10^{-8}$ to $10^{-4}$ M at neutral pH. Optimal measurement conditions for a 50:50 distribution of the Na tracer between the solid and liquid phase would imply that at 0.1 M NaClO₄, ~450 g L⁻¹ of conditioned illite would be required. This is experimentally impossible, and the results of the calculations are given merely for illustrative purposes. A background concentration of $10^{-2}$ M NaClO₄ is a reasonable practical upper limit in such CEC measurements.

Table 8 shows that in the measurement window between $10^{-3}$ and $10^{-2}$ M NaClO₄, even a very low Ca background concentration can have a significant influence on the value of the Na-CEC determinations. Unless Ca (and other bivalent metal) concentrations are measured in the supernatant solutions, the existence of this effect, and its consequences for the Na-CEC value, would be missed.

## SUMMARY AND CONCLUSIONS

The isotope dilution technique is widely used to measure CEC values in clay mineral systems. The advantages of the method are that it is simple and

Table 8. Na occupancies on illite (meq kg⁻¹) calculated as a function of equilibrium Ca concentration for a range of NaClO₄ background electrolyte concentrations. (CEC-PS = 180 meq kg⁻¹; $_{Na}^{Ca}K_c^{PS} = 2$; CEC-type II = 45 meq kg⁻¹; $_{Na}^{Ca}K_c^{II} = 80$).

| Ca conc. | Na background conc. | | |
| | $10^{-3}$ M | $10^{-2}$ M | $10^{-1}$ M |
| --- | --- | --- | --- |
| $10^{-4}$ M | 13 | 102 | 211 |
| $10^{-5}$ M | 39 | 172 | 223 |
| $10^{-6}$ M | 100 | 208 | 225 |
| $10^{-7}$ M | 176 | 222 | 225 |
| $10^{-8}$ M | 214 | 225 | 225 |

quick, but various literature data indicate that there can be significant discrepancies in the CEC values determined, depending on the particular index cation used and its concentration.

Sodium is chosen as index cation in many routine CEC determinations and was selected as the focus of this study on Na-conditioned illite. Experimental determinations of CEC values showed that Cs-CEC > Na-CEC in accord with previous studies. In addition, it was shown experimentally that the Na-CEC increased with increasing $NaClO_4$ concentration. Further, the calculated Ca-Na selectivity coefficient increased by almost an order of magnitude, from 1.6 to 14.3, as the $NaClO_4$ concentration increased from $5.6 \times 10^{-4}$ to 0.1 M. Analyses of supernatant solutions indicated that bivalent cations Ca and Mg were always present at μmolar concentrations no matter how carefully the conditioning process was carried out. Single labeling with $^{45}Ca$ and double-labeling sorption studies with $^{22}Na$ and $^{45}Ca$ demonstrated that residual Ca concentrations as low as $10^{-7}$ M in the conditioned clay mineral systems can lead to significant Ca occupancies on the exchange sites and hence discrepancies in Na-CEC determinations. Since aqueous chemistry data are seldom reported, the influence of low levels of Ca on Na-CEC measurements has not generally been considered. The results presented here indicate that the presence of Ca is probably the main cause of the discrepancies reported in the open literature.

In view of the difficulties with the Na-CEC measurements, a recommendation arising from this work was to use Cs as the index cation *i.e.* a Cs-CEC is determined on a Cs-conditioned illite at a background $CsNO_3$ concentration of $5 \times 10^{-3}$ M, S:L ratio ~20 g $L^{-1}$. The Cs-CEC determined for Illite du Puy in this study was 225 meq $kg^{-1}$ as opposed to the value of 127 meq $kg^{-1}$ given in a previous study (Poinssot *et al.*, 1999a).

A two-site cation-exchange model, with a total CEC = 225 meq $kg^{-1}$, was developed to explain quantitatively the measured differences observed when different index cations are used, the dependency on the Na background electrolyte concentration and the varying values of $^{Ca}_{Na}K_c$ calculated as a function of Na concentration. The parameters in this model were: planar-site capacity = 180 meq $kg^{-1}$, $^{Ca}_{Na}K_c^{PS} = 2$; type II site capacity = 45 meq $kg^{-1}$, $^{Ca}_{Na}K_c^{II} = 80$.

## ACKNOWLEDGMENTS

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